Technical Support Document: Toxicology Clandestine Drug Labs: Methamphetamine

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PHOSPHINE

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Introduction

The clandestine synthesis of methamphetamine (meth) and other illegal drugs is a growing public health and environmental concern. For every pound of meth synthesized there are six or more pounds of hazardous materials or chemicals produced. These are often left on the premises, dumped down local septic systems, or illegally dumped in backyards, open spaces, in ditches along roadways or down municipal sewer systems. In addition to concerns for peace officer safety and health, there is increasing concern about potential health impacts on the public and on unknowing inhabitants, including children and the elderly, who subsequently occupy dwellings where illegal drug labs have been located.

The Office of Environmental Health Hazard Assessment (OEHHA), in cooperation with the Department of Toxic Substances Control (DTSC), has been charged with assisting in identifying and characterizing chemicals used or produced in the illegal manufacturing of methamphetamine, which pose the greatest potential human health concerns. To address in part this growing environmental problem and the need for public health and safety professionals to make appropriate risk management decisions for the remediation of former methamphetamine laboratory sites, OEHHA has developed two types of chemical-specific information documents.

The first set, technical support documents (TSDs), are referenced, multi-page publications, which contain important health and safety data, exposure limits, and key information for recognizing chemicals used or produced during the manufacturing of methamphetamine. These documents will likely be most helpful to health and safety officers, industrial hygienists, or others interested in more detailed toxicological information. The second set, two-page fact sheets, contain much of the same information as the corresponding TSDs; however, the details are presented in a more succinct, graphical format. The fact sheets will be helpful to individuals, including the public, who want to be able to quickly recognize potential chemicals of concern found in illegal methamphetamine labs in order to avoid inadvertent exposures and resulting health impacts.

For more information or to obtain copies of these and other documents, contact:

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I. Chemical Name

A. PHOSPHINE (PH_3)

B. Synonyms

Hydrogen phosphide, phosphorus hydride, phosphorus trihydride.

II. Role in Clandestine Drug Synthesis: Methamphetamine

Phosphine is a by-product generated during the synthesis of hydriodic acid from iodine and red phosphorus (Turkington, 2000). It is produced when red phosphorus contacts caustics and/or acids, especially in the presence of a metal. A number of cooks in clandestine methamphetamine drug labs have died because of inadvertent exposure to phosphine.

III. Chemical Description

A. Appearance

Phosphine is a colorless gas at room temperature (HSDB, 2001).

B. Taste

Not available.

C. Odor

Phosphine is often reported as having a disagreeable, garlic-like odor; like the odor of decaying fish (HSDB, 2001). Pure phosphine is odorless at concentrations up to 200 ppm, a highly toxic level. The characteristic garlic-like odor often attributed to phosphine is actually due to the presence of impurities (IPCS, 1998).

D. Odor Threshold

0.5 ppm (Amoore & Hautala, 1983).

E. Irritancy Threshold

Not available. The odor threshold (0.5 ppm) for phosphine is equivalent to the estimated threshold for irreversible or other serious adverse health effects (AIHA, 2002). Therefore, exposure to a concentration sufficient to cause respiratory irritation would probably result in serious or irreversible effects on health.

F. Odor Safety Class

D (Amoore & Hautala, 1983); only 10-50% of distracted individuals perceive warning of the threshold limit value (TLV) concentration (0.3 ppm). *Therefore, odor is not an adequate indicator of the presence of phosphine and does not provide reliable warning of hazardous concentrations.*

G. Vapor Density

The vapor density of phosphine is 1.2 (air = 1); therefore, phosphine is slightly heavier than air (HSDB, 2001).

H. Vapor Pressure

26,700 mmHg (3560 KPa) (HSDB, 2001).

IV. Containers and Packaging

A. Commercial Products

Aluminum and zinc phosphide release phosphine gas when exposed to moisture and both are used as rodenticides. Aluminum phosphide is also used as a grain fumigant. Commercial pesticides containing aluminum phosphide are Celphos, Phostoxin, and Quick Phos (HSDB, 2001). Phosphine is commonly used in the electronics industry as a dopant for silicon semiconductors (Rickelton, 1995).

B. Pharmaceutical Use

No pharmaceutical use of phosphine gas was identified (USP, 1998).

V. Chemical Hazards

A. Reactivity

Phosphine reacts with many metals, including copper, silver, gold, and the salts of these metals (HSDB, 2001). The commercially available product often reacts spontaneously and violently at room temperature on contact with air due to the presence of other phosphorus hydrides (especially diphosphorus hydride (P_2H_4)) as impurities (IPCS, 1998; NIOSH, 1997). It also reacts violently with oxygen, oxidizers (e.g., nitric acid and nitrogen oxides), metal nitrates, and halogens (fluorine, chlorine, bromine and iodine) causing a fire and explosion hazard (HSDB, 2001; IPCS, 1998; Voltaix, 2001).

B. Flammability

NFPA flammability rating = 4 (very flammable). The lower explosive limit in air = 1.8 % (26 g/m^3). Phosphine is very flammable and potentially explosive. It may ignite spontaneously on contact with air (HSDB, 2001).

C. Chemical Incompatibilities

Phosphine may react spontaneously and violently on contact with air at room temperature (NIOSH, 1997). Phosphine also reacts violently with oxygen, oxidizers (e.g., nitric acid and nitrogen oxides), metal nitrates, halogens (fluorine, chlorine, bromine and iodine), and many other substances creating a fire and explosion hazard (IPCS, 1998).

VI. Health Hazards

A. General

Inhalation of phosphine gas can result in adverse effects on the nervous system, gastrointestinal tract, lungs, and heart. Nervous system effects include fatigue, headache, restlessness, irritability, drowsiness, tremors, dizziness, double vision, and impaired gait (IRIS, 1995; ATSDR, 2000). Gastrointestinal symptoms may include nausea, vomiting, abdominal pain, and diarrhea. Effects on the lungs include chest tightness, cough, and shortness of breath. Severe exposure may lead to accumulation of fluid in the lungs, but the onset of this effect may be delayed by seventy-two hours or more. Other symptoms may include a marked decrease in blood pressure, rapid and/or irregular heartbeat, and cardiac arrest (ATSDR, 2000). Treatment of phosphine

poisoning is generally supportive. There is no specific antidote for this chemical. There are no biological indicators for exposure to phosphine (HSDB, 2001). Therefore, analysis of hair, nails, urine, blood, or exhaled air will not provide evidence of exposure to phosphine.

B. Acute Effects

Acute effects resulting from short-term exposure to high concentrations (greater than approximately 2 ppm) include severe lung irritation, cough, and chest tightness. Onset of severe fluid accumulation in the lungs (pulmonary edema) may be delayed. For this reason, persons with known exposure to phosphine should be hospitalized and observed for seventy-two hours. Neurological effects include dizziness, lethargy, convulsions, and coma. Persons acutely exposed to phosphine often exhibit agitated, psychotic behavior (HSDB, 2001). Signs and symptoms of acute phosphine toxicity include rapid and/or irregular heart rate, low blood pressure, shock, nausea, abdominal pain, vomiting, diarrhea, and cardiac arrest (ATSDR, 2000). Onset of most of the symptoms listed above generally occurs within the first few hours after inhalation exposure; however, the onset of liver and kidney toxicity is delayed (HSDB, 2001).

C. Chronic Effects

Chronic effects resulting from long-term exposure to low concentrations (in a range of approximately 0.5 to 1 ppm) include anemia, bronchitis, gastrointestinal symptoms (nausea, vomiting, abdominal pain, and diarrhea), and neurological effects (tremors, double vision, impaired gait, and difficulty speaking). Liver damage and jaundice, as well as renal failure are also potential consequences of long-term exposure to phosphine gas (HSDB, 2001). Structural changes in chromosomes of peripheral blood cells have been reported in workers exposed occupationally to phosphine. Potential conditions resulting from exposure to phosphine gas over longer periods of time include reactive airway dysfunction syndrome (RADS). RADS is a chemical or irritant-induced type of asthma. Chronic exposures may also cause toothache(s), swelling of the jaw, “phossy jaw” (deterioration of the jaw bone), and spontaneous fractures of bones (IPCS, 1998).

D. Skin Contact

Skin contact with phosphine gas is not likely to be a significant route of exposure unless the concentration in air is high enough to produce adverse health effects by inhalation. If this is the case, respiratory protection should be regarded as the primary consideration; protection of exposed skin would be a secondary concern.

E. Eye Contact

Eye contact with phosphine gas may cause irritation, tearing, pain, swelling, and sensitivity to light (photophobia) (HSDB, 2001).

F. Inhalation

Inhalation of phosphine gas is the primary route of exposure in the majority of clinical and occupational cases. Short-term exposure to high concentrations of phosphine may produce adverse effects on the lungs, nervous system, heart, gastrointestinal tract, liver, and kidneys. Typical early symptoms include irritation of mucous membranes, cough, and shortness of breath; pulmonary edema may occur with delayed onset. Potential adverse effects on the nervous system include dizziness, headache, fatigue, restlessness, difficulty walking, and seizures. Agitated psychotic behavior may also occur (HSDB, 2001). Additional symptoms are described above in section VII, B. Symptoms resulting from long-term (>6 months) exposure to lower

concentrations of phosphine gas (approximately 0.5 to 2 ppm) include cough, difficulty breathing, headache, giddiness, numbness, lethargy, diminished appetite, and intestinal pain.

G. Ingestion

Ingestion of certain types of waste generated by clandestine methamphetamine labs may result in the release of phosphine gas in the stomach. Likely symptoms of chemicals that produce phosphine internally when ingested include abdominal pain, nausea, vomiting, and diarrhea (ATSDR, 2000).

H. Predisposing Conditions

Predisposing conditions that would have the potential to increase susceptibility to phosphine include compromised function of any of the organ systems affected by phosphine. Therefore, persons with compromised function of the lungs, nervous system, gastrointestinal tract, heart, liver, or kidneys potentially would be more sensitive to the toxicity of phosphine. For example, emphysema or other types of chronic lung disease are likely to be more susceptible to the adverse effects of phosphine on the lungs. Persons with weakened bones (e.g., osteoporosis) may also be more sensitive to chronic phosphine exposure.

I. Special Concerns for Children

Compared to adults, children have a greater ratio of lung surface area to body weight. Similarly, the ratio of respiratory minute volume to body weight is greater in children than adults. Therefore, at any given concentration of phosphine in air, children will probably receive a larger dose than adults. In addition, the vapor density of phosphine is greater than that of air. Therefore, higher concentrations of phosphine are likely to be found closer to the ground. Children may be exposed to higher concentrations of phosphine gas than adults because of their short stature. Children may be more sensitive to inhaled phosphine because of the smaller diameter of their airways. Therefore, if the inhaled dose is sufficient to cause swelling or spasms of the larynx, upper airway obstruction and asphyxia are more likely to occur in children. Children may be more susceptible to the toxic effects of phosphine because they may not understand they are in danger and may be less likely to leave an area where a release has occurred.

VII. First Aid

A. Eyes

Flush eyes with water for at least thirty minutes. Get medical attention immediately (Voltaix, 2001).

B. Skin

Remove contaminated clothing and flush skin with plenty of water for at least fifteen minutes. Get medical attention immediately (Voltaix, 2001).

C. Ingestion

Do not induce vomiting. Get medical attention immediately (HSDB, 2001).

D. Inhalation

Get medical attention immediately (Voltaix, 2001). If victim is not breathing, give artificial respiration. If victim has difficulty breathing, administer oxygen. Symptoms of swelling in the

lungs (edema) often do not become apparent until a few hours after exposure and are aggravated by physical effort (IPCS, 1998). Medical observation and rest are essential.

VIII. Standards for Inhalation Exposure

A. Occupational Exposure Limits (NIOSH, 1997; ACGIH, 1994)

1. Ceiling Limit (C) (not to be exceeded at any time): Not established.
2. Short-Term Exposure Limit (STEL or ST): 1 ppm (1.4 mg/m^3)
3. 8-Hour Time Weighted Average (TWA): 0.3 ppm (0.4 mg/m^3)
4. 10-Hour Time Weighted Average (TWA): 0.3 ppm (0.4 mg/m^3)
5. Immediately Dangerous to Life & Health (IDLH): 50 ppm (70 mg/m^3)

Important Definitions Follow:

Ceiling Limit (C) is a concentration that must not be exceeded during any part of the workday.

Short-Term Exposure Limit (STEL or ST) is a 15-minute time-weighted average concentration that should not be exceeded during any part of the workday.

8-Hour Time Weighted Average (8-hour TWA) concentration is an exposure standard that must not be exceeded during any 8-hour work shift of a 40-hour workweek. 8-Hour TWA exposure standards established by the Occupational Safety and Health Administration (OSHA) are called Permissible Exposure Limits (PELs). 8-Hour TWA exposure standards established by the American Conference of Governmental Industrial Hygienists (ACGIH) are called Threshold Limit Values (TLVs).

10-Hour Time Weighted Average (10-hour TWA) concentration is an exposure standard that must not be exceeded during a 10-hour workday of a 40-hour workweek. 10-Hour TWA exposure standards developed by the National Institute for Occupational Safety and Health (NIOSH) are called Recommended Exposure Limits (RELs).

Immediately Dangerous to Life & Health (IDLH) defines a concentration which poses a threat of death or immediate or delayed permanent health effects, or is likely to prevent escape from such an environment in the event of failure of respiratory protection equipment. IDLH values are developed by the National Institute for Occupational Safety and Health (NIOSH).

"Skin" notation (NIOSH): significant uptake may occur as a result of skin contact. Therefore, appropriate personal protective clothing should be worn to prevent dermal exposure.

B. Emergency Response Planning Guidelines (1 hour or less) (AIHA, 2002)

1. ERPG-1 (protective against mild, transient effects): Not appropriate.
2. ERPG-2 (protective against serious adverse effects): 0.5 ppm (0.7 mg/m^3)
3. ERPG-3 (protective against life-threatening effects): 5ppm (7 mg/m^3)

NOTE: There is a significant discrepancy between the IDLH concentration (50 ppm) and the ERPG-3 concentration (5 ppm). Both values are intended to provide an estimate of a life-threatening concentration. Given the lack of human toxicity data for lethality of phosphine, OEHHA recommends using the ERPG-3 value as an estimate of a potential lethal concentration.

Emergency Response Planning Guidelines (ERPGs) are developed by the American Industrial Hygiene Association (AIHA) to assist in planning and preparation for catastrophic accidental chemical releases. ERPGs allow emergency response planners to estimate the consequences of large-scale chemical releases on human health, and evaluate the effectiveness of prevention strategies and response capabilities. ERPGs assume that the duration of exposure is one hour or less. They are not intended to be used as limits for routine operations and are not legally enforceable.

Definitions for the three ERPG levels are:

ERPG-1: an estimate of the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing more than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor.

ERPG-2: an estimate of the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.

ERPG-3: an estimate of the maximum airborne concentration below which nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

C. Acute Reference Exposure Level (1-hour exposure) (OEHHA, 1999)

Level protective against mild adverse effects: Not established.

D. Chronic Reference Exposure Level (multiple years) (OEHHA, 2002)

Level protective of adverse health effects: 0.6 ppb (0.8 µg/m^3)

Reference Exposure Levels (RELs) are developed by the California EPA's Office of Environmental Health Hazard Assessment (OEHHA). A REL is a concentration at or below which no adverse health effects are anticipated, even in the most sensitive members of the general population (for example, persons with pre-existing respiratory disease). RELs incorporate uncertainty factors to account for information gaps and uncertainties in the toxicological data. Therefore, exceeding a REL does not necessarily indicate an adverse health impact will occur in an exposed population. Acute RELs are based on an assumption that the duration of exposure is one hour or less. Chronic RELs are intended to be protective for individuals exposed continuously over at least a significant fraction of a lifetime (defined as 12 years).

E. Chronic Reference Concentration (lifetime exposure) (IRIS, 1995)

Level protective of adverse health effects: 3.0×10^{-4} mg/m^3

IX. Environmental Contamination Concerns

A. Surface Water

Due to its extreme volatility, any release of phosphine to surface water would quickly evaporate to the surrounding air.

B. Groundwater

Phosphine is extremely volatile and is released to air during clandestine methamphetamine synthesis. Waste generated by clandestine laboratories may produce small amounts of phosphine, but the small amount potentially released to soil would not be sufficient to cause contamination of groundwater. However, large amounts of buried phosphorus-containing waste may represent a significant source of soil and groundwater contamination.

C. Drinking Water

No information available.

Suggested No Adverse Response Level (NAS, 1980): Not established.

Preliminary Remediation Goal for Tap Water (U.S. EPA, 2002 Region IX): 11 ppb (11 μg/l)

D. Soil

The amount of phosphine gas produced by a typical clandestine laboratory does not represent a significant threat to soil and groundwater. Phosphine is a gas at room temperature, and any residue of phosphine present in a solid or liquid waste would quickly evaporate under most circumstances. However, large amounts of buried phosphorus-containing waste may represent a significant source of soil and groundwater contamination. Phosphine is removed from trapped air in soil by soil components through oxidization to orthophosphate (IPCS, 1989).

Preliminary Remediation Goal for Residential Soil (U.S. EPA, 2002 Region IX):

18 ppm (18 mg/kg)

E. Air

In the atmosphere, phosphine exists solely as a gas. In the troposphere, phosphine reacts primarily with hydroxyl radicals; eventual products are water and phosphorus oxyacids (IPCS, 1989). Based on this reaction, the atmospheric half-life and lifetime of phosphine are calculated to be 0.7 and 1 day, respectively (ARB, 1997). Phosphine would also be expected to react with water vapor in the air. Phosphine is removed from air by soil and oxidized to orthophosphate (IPCS, 1989).

Preliminary Remediation Goal for Ambient Air (U.S. EPA, 2002 Region IX): 0.2 ppb (0.3 μg/m^3)

F. Indoor Surface Contamination

Since phosphine is a gas at room temperature, residues of phosphine will not accumulate on indoor surfaces.

G. Natural Occurrence and/or Abundance

Phosphine is formed in small amounts from the putrefaction of organic matter containing phosphorus (Merck, 1976). Therefore, detection of low concentrations of phosphine in sewers or septic systems would not be unexpected.

X. Personal Protective Equipment

Wear a positive pressure, full facepiece, supplied air breathing apparatus and neoprene gloves (Voltaix, 2001).

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